## ENGINEERING DATA BOOK

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#### **SECTION 22**

# Sulfur Recovery

Sulfur is present in natural gas principally as hydrogen sulfide (H<sub>2</sub>S) and, in other fossil fuels, as sulfur-containing compounds which are converted to hydrogen sulfide during processing. The H<sub>2</sub>S, together with some or all of any carbon dioxide (CO<sub>2</sub>) present, is removed from the natural gas or refinery gas by means of one of the gas treating processes described in Section 21. The resulting H<sub>2</sub>S-containing acid gas stream is flared, incinerated, or fed to a sulfur recovery unit. This section is concerned with recovery of sulfur by means of the modified Claus and Claus tail gas clean-up processes. Redox processes are touched upon. For a discussion and description of other sulfur recovery processes, see Maddox<sup>1</sup>.

#### THE CLAUS PROCESS

The Claus process as used today is a modification of a process first used in 1883 in which  $H_2S$  was reacted over a catalyst with air (oxygen) to form elemental sulfur and water.

$$H_2S + \frac{1}{2}O_2 \rightarrow S + H_2O$$
 Eq 22-1

Control of this highly exothermic reaction was difficult and sulfur recovery efficiencies were low. In order to overcome these process deficiencies, a modification of the Claus process was developed and introduced in 1936 in which the overall reaction was separated into (1) a highly exothermic thermal or combustion reaction section in which most of the overall heat of reaction (from burning one-third of the H<sub>2</sub>S and essentially 100% of any hydrocarbons and other combustibles in the feed) is released and removed, and (2) a moderately exothermic catalytic reaction section in which sulfur dioxide (SO<sub>2</sub>) formed in the combustion section reacts with unburned H<sub>2</sub>S to form elemental sulfur. The principal reactions taking place (neglecting those of the hydrocarbons and other combustibles) can then be written as follows:

Thermal or Combustion Reaction Section

$$H_2S + 1\frac{1}{2}O_2 \rightarrow SO_2 + H_2O$$
 Eq 22-2  
 $\Delta H @ 77^{\circ}F = -223\ 100\ Btu$ 

Combustion and Catalytic Reaction Sections

$$2 H_2S + SO_2 \rightarrow \frac{3}{x} S_x - 2 H_2O$$
 Eq 22-3

 $\Delta H @ 77^{\circ}F = -41\ 300\ Btu$ 

Overall Reaction

 $3 H_2S + 1\frac{1}{2}O_2 \rightarrow \frac{3}{x}S_x + 3 H_2O$  Eq 22-4

 $\Delta H @ 77^{\circ}F = -264 400 Btu$ 

This is a simplified interpretation of the reaction actually taking place in a Claus unit. The reaction equilibrium is complicated by the existence of various species of gaseous sulfur  $(S_2, S_3, S_4, S_5, S_6, S_7, \text{ and } S_5)$  whose equilibrium concentrations in relation to each other are not precisely known for the entire range of process conditions. Furthermore, side reactions involving hydrocarbons,  $H_2S$ , and  $CO_2$  present in the acid gas feed can result in the formation of carbonyl sulfide (COS), carbon disulfide (CS<sub>2</sub>), carbon monoxide (CO), and hydrogen (H<sub>2</sub>). Gamson and Elkins<sup>2</sup> cover the basic theory involved in the Claus process; however, they ignore the many potential side reactions and also the existence of  $S_3$ ,  $S_4$ ,  $S_5$ , and  $S_7$ .

For the usual Claus plant feed gas composition (water-saturated with 30-80 mol %  $H_2S$ , 0.5-1.5 mol % hydrocarbons, the remainder  $CO_2$ ), the modified Claus process arrangement results in thermal section (burner) temperatures of about 1800 to 2500°F. The principal molecular species in this temperature range is  $S_2$  (Fig. 22-19) and conditions appear favorable for the

FIG. 22-1

#### Nomenclature

H = heat content or enthalpy, Btu/lb or Btu/lb-mole

K<sub>p</sub> = equilibrium constant

For the low pressure, vapor phase Claus reaction

$$2 H_{2}S + SO_{2} \rightarrow 2 H_{2}O + \frac{3}{x} S_{x}$$

$$K_{p} = \frac{(P_{H_{2}O})^{3} (P_{S_{x}})^{3/x}}{(P_{H_{2}S})^{2} (P_{SO_{x}})}$$

$$= \frac{[Mols H_{2}O]^{3} [Mols S_{x}]^{3/x}}{[Mols H_{2}S]^{2} [Mols SO_{2}]} \left[\frac{\pi}{\text{Total Mols}}\right]^{\frac{3}{x}-1}$$

LT/D = long ton per day. A long ton is 2240 pounds.

P = partial pressure, atmospheres

 $\pi$  = total pressure, atmospheres

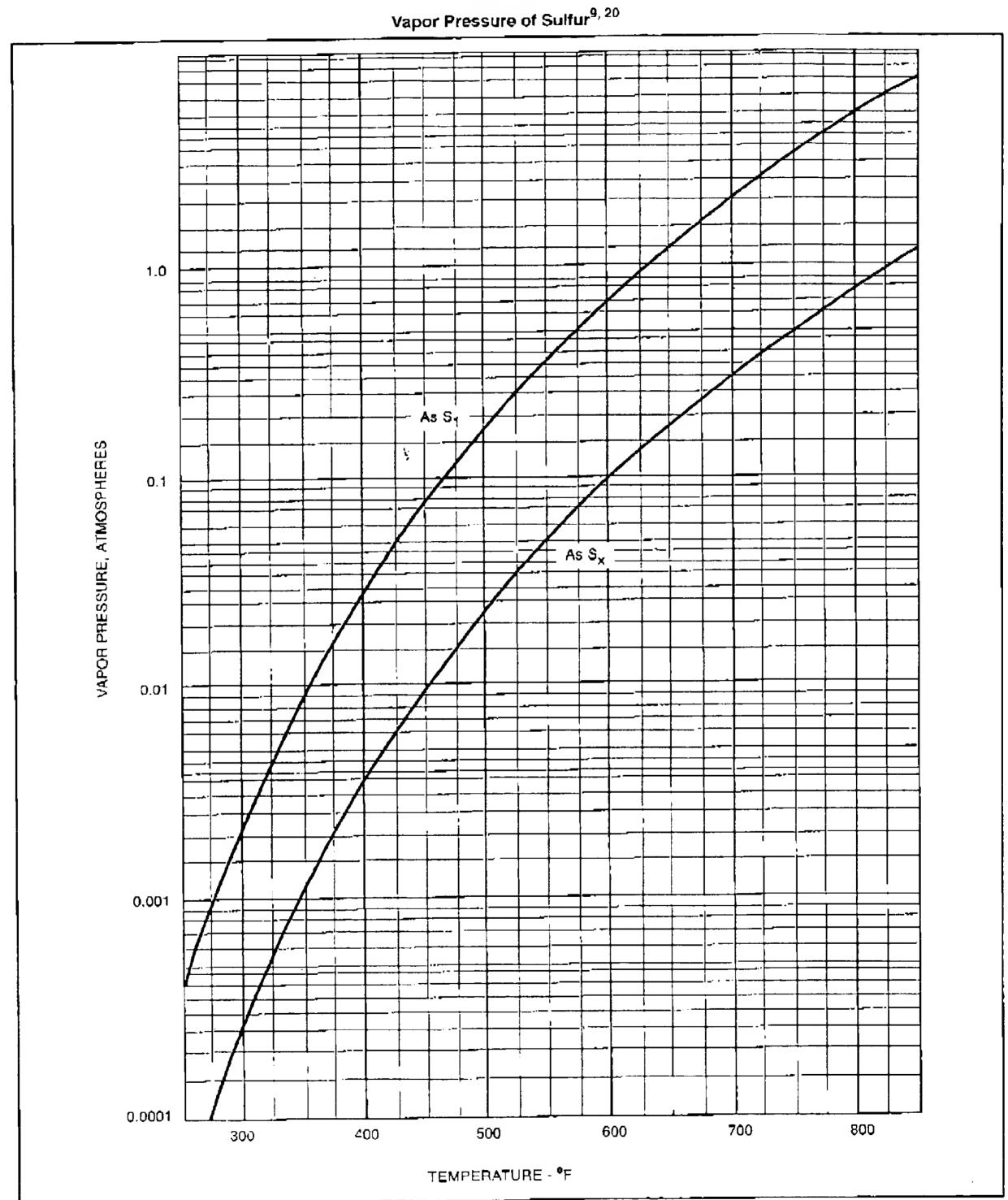
Acid Gas: feed stream to sulfur recovery plant consisting of H<sub>2</sub>S, CO<sub>2</sub>, H<sub>2</sub>O, and usually less than 2 mol % hydrocarbons.

Claus Process: a process in which  $\frac{1}{3}$  of the H<sub>2</sub>S in the acid gas feed is burned to SO<sub>2</sub> which is then reacted with the remaining H<sub>2</sub>S to produce sulfur. This is also referred to as the modified Claus process.

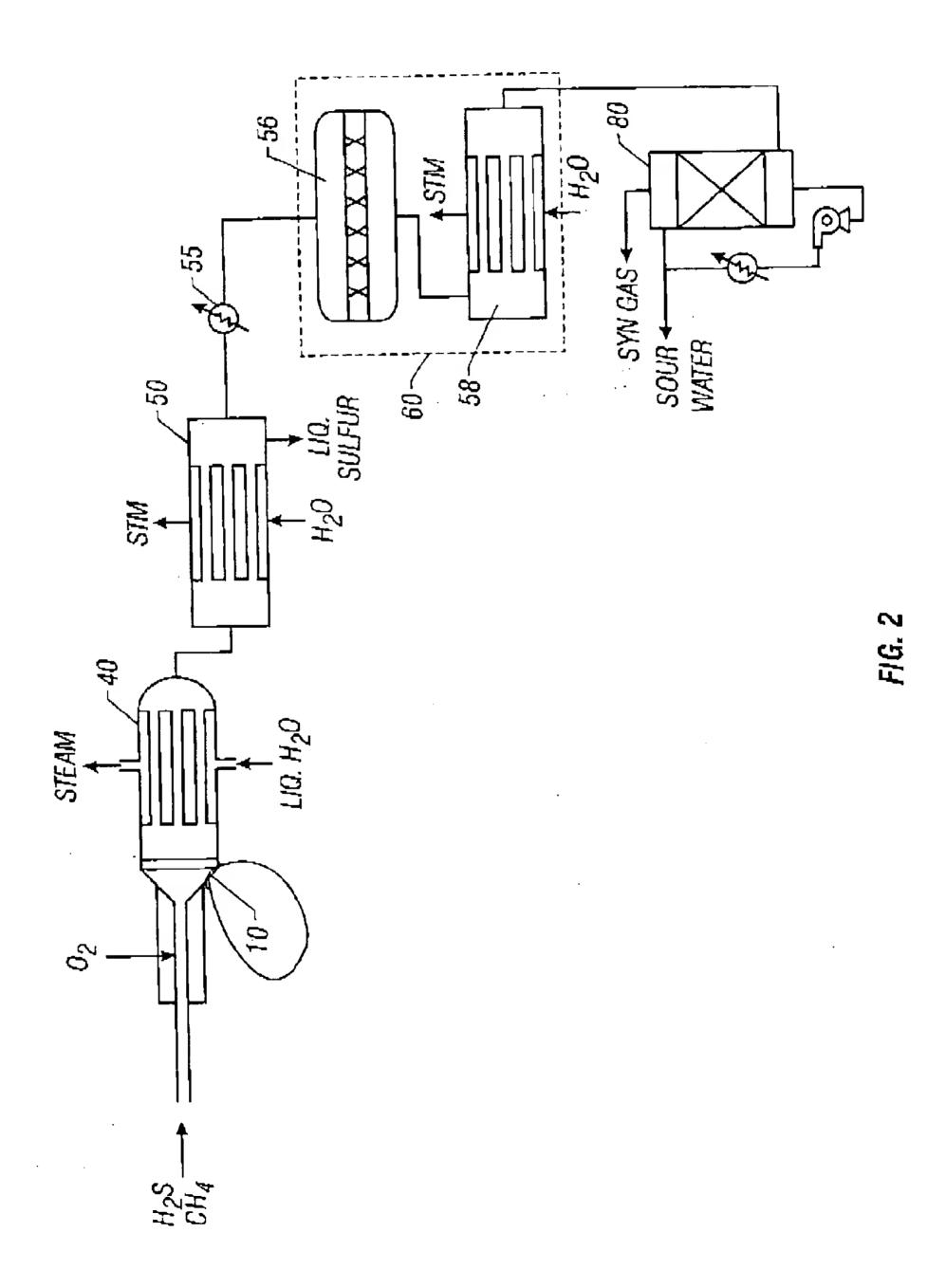
Residence Time: the period of time in which a process stream will be contained within a certain volume or piece of equipment, seconds.

Tail Gas Cleanup Unit: a process unit designed to take tail gas from a Claus sulfur recovery plant and remove additional sulfur with the goal of meeting environmental sulfur emission standards.

FIG. 22-20



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Amdt. Dated August 28, 2003
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Annotated Sheet Showing Changes



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